[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Kinetics of the Acid-catalyzed Isomerization of Neoabietic Acid in Anhydrous Ethanol

BY PAUL F. RITCHIE AND LANE F. MCBURNEY

Treatment of oleoresin with acids or heat results in an increase of the abietic acid content of the initial material. The constituents of oleoresin which are involved in this reaction are the three isomeric resin acids: abietic, neoabietic and levopimaric. In a previous paper[1] the kinetics of the acid-catalyzed isomerization of levopimaric acid in anhydrous ethanol was discussed. The present communication is the result of a similar study of the isomerization of neoabietic acid.

Experimental Details

Neoabietic acid was isolated from the oleoresin of *Pinus palustris* by the amine salt technique of Harris and Sanderson.[2] After recrystallization from alcohol and water to constant rotation (c = 1%, ethanol) $[\alpha]^{24}\text{D}$ + 159° the neoabietic acid was dried in the vacuum oven at 60° for four hours.

Hydrogen bromide was prepared by dropping bromine into an all-glass generator containing freshly distilled tetralin.[3] The evolved hydrogen bromide was purified from traces of bromine by passage through two scrubbing bottles containing tetralin. Removal of tetralin and moisture was accomplished by passing the gas through a trap maintained at −55° and a calcium chloride tube. After thoroughly flushing the apparatus with a stream of hydrogen bromide, an absorption flask containing anhydrous ethanol was connected to the outlet. Absorption of the gas was continued until the increase in weight indicated that the concentration of hydrogen bromide in the solution was near that desired. The acidity of the solution was accurately determined by titration of weighed samples with standard sodium hydroxide solution using methyl red as the indicator.

The preparation and purification of all other materials used, the apparatus, and the experimental method have been adequately described in a previous communication.[1]

The course of the reaction was followed in the manner described by Guggenheim,[4] and the constants of the general first-order expression $\log (\alpha - \alpha') = a - kt \log e$ were calculated from the experimental data by the method of averages. Table I contains the data obtained from a typical experiment, the rate expression, the values computed for $(\alpha - \alpha')$, and the differences $\Delta (\alpha - \alpha')$ between the observed and calculated values of $(\alpha - \alpha')$. The mean deviation amounts to about 2% of the smallest observed value of $(\alpha - \alpha')$.

TABLE I

ACID-CATALYZED ISOMERIZATION OF NEOABIETIC ACID,[a] $\log (\alpha - \alpha') = 0.818 - 0.00363t$

t, min.	α	$t + \Delta t$, min.	α'	$(\alpha - \alpha')$ Obsd.	$(\alpha - \alpha')$ Calcd.	$\Delta (\alpha - \alpha')$
6	(+) 6.18°	116	(+) 0.01°	(+) 6.17°	(+) 6.25°	+0.08°
16	5.38	126	(−) 0.29	5.67	5.75	+ .08
26	4.69	136	0.61	5.30	5.29	− .01
36	3.94	146	0.93	4.87	4.86	− .01
46	3.30	156	1.22	4.52	4.48	− .04
56	2.75	166	1.45	4.20	4.12	− .08
66	2.16	176	1.60	3.76	3.78	+ .02
76	1.58	186	1.80	3.38	3.48	+ .10
86	1.19	196	2.00	3.19	3.20	+ .01
96	0.78	206	2.20	2.98	2.95	− .03
106	0.42	216	2.37	2.79	2.71	− .08
					Mean deviation	± .05

[a] Concentration of reactants in moles per liter; neoabietic acid, 2.99×10^{-2}; hydrogen chloride, 4.50×10^{-2}.

Probable errors in the velocity constants were calculated and are represented by the radii of the circles in the graphs which follow. Unless otherwise specified all measurements were made at 25°.

Results and Discussion

While the rotatory power of ethanolic solutions of neoabietic acid remains unaltered at the initial value of $\alpha^{24}\text{D}$ + 159°[2] for periods of at least several days, in the presence of a strong acid catalyst the specific rotation of the solutions changes quite rapidly to an equilibrium value of about −90°. Although it was found that the change proceeded in strict accord with first-order kinetics over most of its course, there were indications that slight deviations from the first-order course occurred after the reaction had reached about 85% completion. This observation, together with the fact that the reaction solutions acquired considerable color after standing for several hours, suggests that during the late stages of the isomerization a side reaction of unknown nature assumes some importance. The equilibrium value of the specific rotation (−90°) and ultraviolet absorption spectra of solutions of isomerized neoabietic acid were identical with those previously reported for solutions of acid-isomerized levopimaric acid.[1] The spectra showed that over 90% of the original neoabietic acid had been converted to abietic acid but afforded no indication of the presence of either neoabietic or levopimaric acid in the equilibrium mixture. However, the presence of levopimaric acid in the equilibrium mixture is proved by the fact that the same adduct, that of levopimaric acid, is formed when maleic anhydride reacts with acidified solutions of abietic, neoabietic or levopimaric acid.[5]

Table II contains data obtained from a series of experiments in which the velocity of isomerization was measured at various initial concentrations of neoabietic acid and at a constant concentration of the catalyst, hydrogen chloride. The results indicate that the velocity constant is independent of the initial concentration of the resin acid.

The results of experiments in which the velocity of isomerization of neoabietic acid in ethanol

---

(1) P. F. Ritchie and L. F. McBurney, THIS JOURNAL, **71**, 3736 (1949).

(2) G. C. Harris and T. F. Sanderson, *ibid.*, **70**, 334 (1948).

(3) D. R. Duncan, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, Inc., New York, N. Y., 1939, p. 151.

(4) E. A. Guggenheim, *Phil. Mag.*, I, 538 (1926).

(5) G. C. Harris, THIS JOURNAL, **70**, 3671 (1948).

TABLE II

VELOCITY OF ISOMERIZATION AT VARIOUS INITIAL CONCENTRATIONS OF NEOABIETIC ACID[a]

Neoabietic acid, moles/liter × 10^2	Reaction velocity $k \times 10^3$ (min.$^{-1}$)
1.47	5.69
1.66	5.14
2.98	5.85
4.97	5.25
6.94	5.72

[a] Concentration of hydrogen chloride, 3.61 × 10^{-2} moles/liter.

containing varying amounts of the strong acids, hydrogen chloride, hydrogen bromide, *p*-toluenesulfonic acid and methanesulfonic acid are assembled in Table III. In Fig. 1 the data obtained with hydrogen chloride and hydrogen bromide are expressed in graphical form as the plots of k/c *versus* c, k being the reaction velocity and c the catalyst concentration. The linear dependence of k/c upon c is in agreement with Brönsted's[6] theory of primary electrolyte effects. Further evidence for the existence of a primary salt effect was acquired by measurement of the velocity of isomerization in solutions containing constant amounts of hydrogen chloride and neoabietic acid but varying amounts of the neutral electrolyte lithium chloride (Fig. 2).

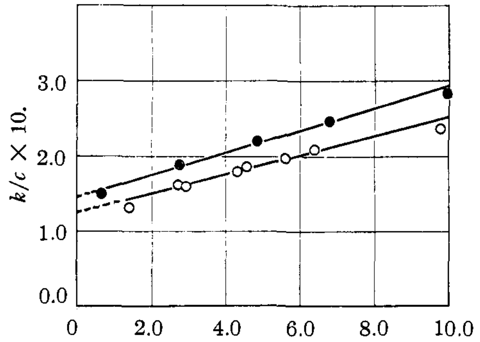


Fig. 1.—Isomerization of neoabietic acid catalyzed by (○) hydrogen chloride and (●) hydrogen bromide: k is the reaction velocity and c the catalyst concentration in moles/liter; concentration of neoabietic acid, 3.30 × 10^{-2} mole/liter.

Extrapolation of the curves of Fig. 1 leads to values of k/c, in liters mole^{-1} min.$^{-1}$, at infinite dilution with respect to hydrogen chloride (1.18 × 10^{-1}) and hydrogen bromide (1.45 × 10^{-1}) which are in reasonably good agreement. The conductivity measurements of Murray-Rust and Hartley[7] and Deyrup's studies of acetal formation[8] indicated that hydrogen chloride and hydrogen bromide, at concentrations somewhat lower than those employed in these experiments, are dissociated completely in ethanol. Assuming that dissociation of hydrogen chloride and hydrogen bromide is complete at concentrations of 0.01 to 0.1 mole/liter, agreement of the extrapolated values of k/c may be considered as evidence that the isomerization of neoabietic acid is catalyzed exclusively by the solvated proton $C_2H_5OH_2^+$. The mean of the k/c values at zero concentration of hydrogen chloride and hydrogen bromide (1.31 × 10^{-1}) then becomes an evaluation of the catalytic coefficient $k_{C_2H_5OH_2^+}$ for this reaction. The isomerization of neoabietic acid is not catalyzed at a measurable rate at 25° by one of the strongest of incompletely dissociated acids, trichloroacetic acid. Consequently, it was not possible to prove unequivocally that the solvated proton is the exclusive catalytic species by experiments in buffer solutions.

TABLE III

ISOMERIZATION OF NEOABIETIC ACID CATALYZED BY STRONG ACIDS[a]

	Catalyst concn., moles/liter × 10^2	Reaction velocity, $k \times 10^3$ (min.$^{-1}$)
Hydrogen chloride	1.34	1.64
	2.72	4.40
	2.83	4.53
	4.22	7.55
	4.50	8.36
	5.55	10.9
	6.30	13.1
	9.71	22.9
Hydrogen bromide	0.66	1.01
	2.72	5.13
	4.79	10.5
	6.70	16.5
	9.92	27.9
p-Toluenesulfonic acid	2.83	0.67
	6.96	1.85
	13.6	4.08
	20.1	6.55
Methanesulfonic acid	3.33	0.55
	12.2	2.13
	17.1	3.08
	25.4	4.85

[a] Concentration of neoabietic acid, 3.30 × 10^{-2} moles/liter.

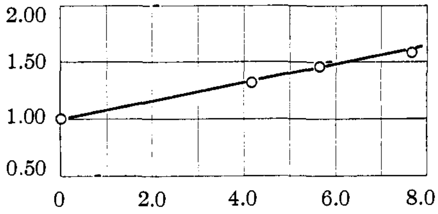


Fig. 2.—Neutral salt effect in the hydrogen chloride-catalyzed isomerization of neoabietic acid: k/k_0 is the ratio of reaction velocities at concentrations c and zero; concentrations of reactants in moles/liter: hydrogen chloride, 1.69 × 10^{-2}; neoabietic acid, 3.33 × 10^{-2}.

---

(6) J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

(7) D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (*London*), **A126**, 86 (1929).

(8) A. J. Deyrup, THIS JOURNAL, **56**, 60 (1934).

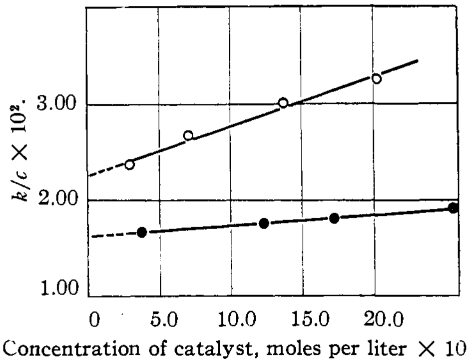


Fig. 3.—Isomerization of neoabietic acid catalyzed by (○) *p*-toluenesulfonic and (●) methanesulfonic acids: *k* is the velocity of reaction and *c* the catalyst concentration in moles/liter; concentration of neoabietic acid, 3.30 × 10^{-2} mole/liter.

Extrapolation of the curves of Fig. 3 yields values of *k*/*c* for methanesulfonic acid (1.61 × 10^{-2}) and *p*-toluenesulfonic acid (2.26 × 10^{-2}) which are significantly lower than those obtained with hydrogen chloride and hydrogen bromide. A similar observation was made in the study of the isomerization of levopimaric acid. Hence it appears that the sulfonic acids employed in the present experiments are incompletely dissociated in ethanol at concentrations greater than 0.01 mole/liter. However, if this is the case, the linear dependence of *k*/*c* upon *c* cannot be safely regarded as a linear salt effect alone since the effect of change of concentration upon the extent of dissociation of the acids is unknown and catalysis by molecular acids is not excluded. Therefore reliable values for the degrees of dissociation of the sulfonic acids concerned cannot be obtained from these data.

Both hydrogen chloride and *p*-toluenesulfonic acid were employed as catalysts in measuring the temperature coefficient of the isomerization of neoabietic acid over the temperature range 20 to 45° (Fig. 4). It was found that the energy of activation of the reaction (21.4 ± 0.5 kcal./mole) is independent of the nature of the strong acid catalyst as would be anticipated in the case of a reaction catalyzed exclusively by solvated protons.

The presence of small amounts of water in the medium greatly inhibits the isomerization of neoabietic acid (Fig. 5). Similar behavior was observed and discussed in connection with the study of the isomerization of levopimaric acid.[1] These observations and the results of many published researches[9,10] fully emphasize the necessity of maintaining absolutely anhydrous conditions when examining the kinetics of catalyzed reactions in non-aqueous systems given.

It was demonstrated in the previous communication[1] that the isomerization of levopimaric acid is catalyzed exclusively by the solvated proton. The evidence, although of an equivocal nature, indicates that the isomerization of neoabietic acid is similarly catalyzed. Both reactions are first order with respect to the catalyst and the resin acids.

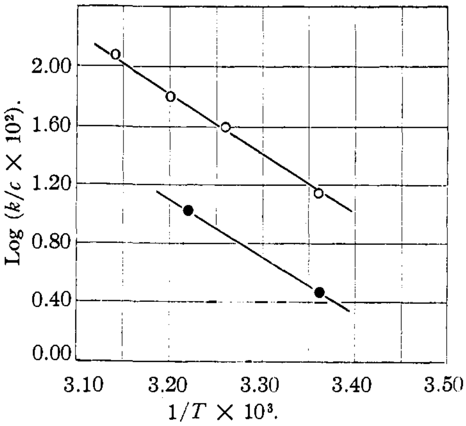


Fig. 4.—Temperature coefficient of the isomerization of neoabietic acid catalyzed by (○) hydrogen chloride and (●) *p*-toluenesulfonic acid: *k* is the reaction velocity, *c* the catalyst concentration in moles/liter and *T* the temperature (°K.); concentration of reactants in moles/liter × 10^2: hydrogen chloride, 1.69; *p*-toluenesulfonic acid, 13.6; neoabietic acid, 3.32.

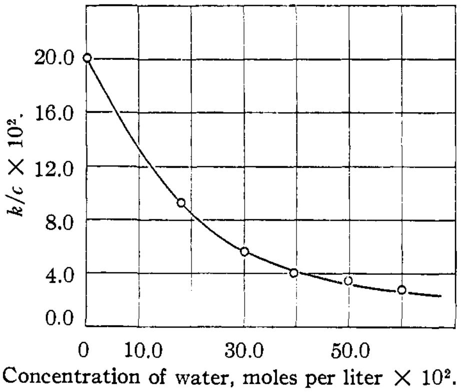


Fig. 5.—Inhibition by water of the hydrogen chloride-catalyzed isomerization of neoabietic acid: *k* is the reaction velocity and *c* the catalyst concentration in moles/liter; concentration of reactants in moles/liter × 10^2; hydrogen chloride, 5.75; neoabietic acid, 3.31.

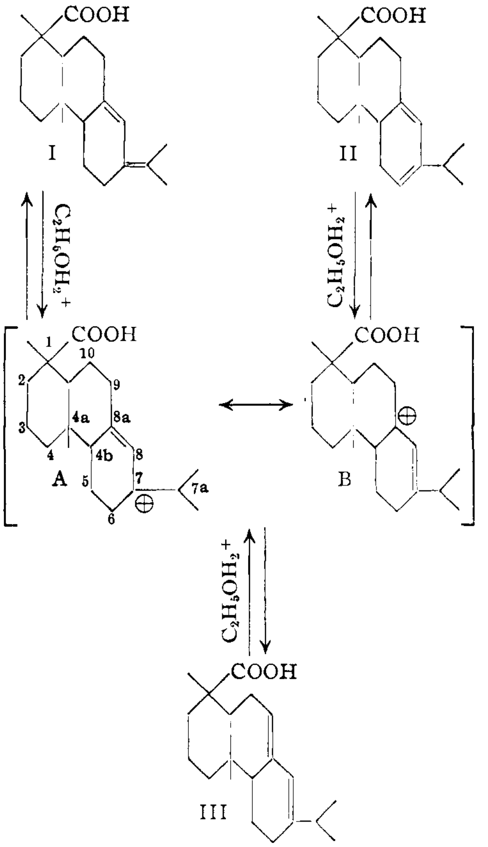
In both cases the same activation energy is involved and the same equilibrium mixture is formed. These conclusions can be adequately explained by the reaction mechanism given.

The rate-controlling step in the reaction is the addition of a solvated proton to either neoabietic acid (I) or levopimaric acid (II) to form the intermediate complex which has been depicted as a resonance hybrid of the two forms A and B. The stability of this intermediate complex can be understood since both components are tertiary carbonium ions.

---

(9) E. A. Braude, *J. Chem. Soc.*, 443 (1944).

(10) G. Bredig and W. Fraenkel, *Ber.*, **39**, 1756 (1906).



Form A can lose its charge by expulsion of a proton from either position 6 or 7a. If this expulsion occurs at position 6, levopimaric acid is regenerated, and if it occurs at 7a, neoabietic acid is regenerated. In neither case does isomerization result. On the other hand, form B can lose its charge by expelling a proton at position 9 or 4b. When position 9 is involved, the result is the formation of abietic acid (III) but if 4b were involved, a new resin acid would be formed. No evidence has been found for the existence of such a new resin acid, and since conjugation between two rings seems to be favored over conjugation within one ring, it is assumed that expulsion of a proton from position 9 is favored. The fact that the final equilibrium mixture contains over 90% abietic acid as shown by the ultraviolet absorption spectra is in agreement with this assumption.

Acknowledgment.—The authors wish to express their thanks to Dr. George C. Harris of these laboratories who supplied the neoabietic acid used during the course of this research.

Summary

Neoabietic acid is converted by ethanolic solutions of strong acids into a mixture consisting chiefly of abietic acid but containing small amounts of levopimaric acid. Ultraviolet absorption spectra afford no indication of the presence of neoabietic or levopimaric acid in the reaction mixture.

The isomerization of neoabietic acid in ethanol appears to be catalyzed exclusively by the solvated proton. Assuming complete dissociation of hydrogen chloride and hydrogen bromide at concentrations of 0.01 to 0.1 mole/liter the catalytic coefficient of the reaction (in liters mole^{-1} min.$^{-1}$) is given by the expression $k_{C_2H_5OH_2^+} = 6.3 \times 10^{14}\ e^{-21,450/RT}$. Small amounts of water in the medium seriously inhibit the reaction.

Data obtained by measurement of the velocity of isomerization at various concentrations of the strong acids, hydrogen chloride and hydrogen bromide, are in good agreement with the Brönsted theory of primary electrolyte effects. The two sulfonic acids seem to be incompletely dissociated in ethanol at the concentration employed in these experiments.

Wilmington 99, Delaware Received August 4, 1949

[Contribution from the Institute of Polymer Research, Polytechnic Institute of Brooklyn]

The Preparation of *p*-Acyloxystyrenes[1]

By C. G. Overberger, Evelyn J. Luhrs and P. K. Chien

We have undertaken the preparation of monomers[2] that contain straight-chain alkyl groups which when polymerized give a polymer with this alkyl group in the side chain. In particular, the formation of crystallites[3] in such a side chain and the influence of this crystallization on the polymer properties are of special interest.

This paper will describe a convenient preparation of some *p*-acyloxystyrenes (II) in which R is a straight-chain alkyl group. The procedure is outlined below. With the exception of R = CH_3, the substituted cinnamic acids (I) and the styrenes have not been previously described. *p*-Acetoxystyrene[4] has previously been prepared by dehydroacetylation of the diacetate of *p*-hydroxyphenylmethylcarbinol and by the dehydration[5] of *p*-(α-hydroxyethyl)-phenyl acetate. The method used, the decarboxylation of a

---

(1) A portion of theses by Evelyn Luhrs and P. K. Chien submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.

(2) Overberger and Roberts, This Journal, **71**, 3618 (1949).

(3) Kaufman, Sacher, Alfrey and Fankuchen, *ibid.*, **70**, 3146 (1948).

(4) Alderman and Hanford, U. S. Patent 2,276,138, March, 1942.

(5) Emerson, Heyd, Lucas, Cook, Owens and Shortridge, This Journal, **68**, 1665 (1946).